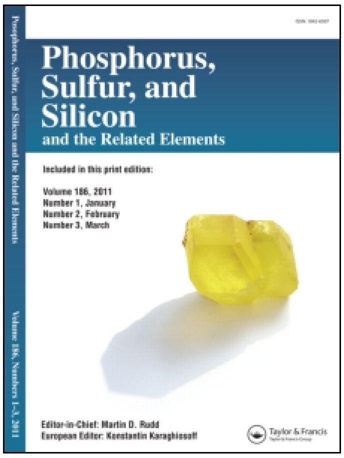

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Issa M. El-Nahhal[a]; Basheer A. El-Shetary[b]; Kamal A. R. Salib[b]; Nizam M. El-Ashgar[a]; Ahmed M. El-Hashash[a]
[a] Department of Chemistry, Al-Azhar University, Gaza, Palestine [b] Department of Chemistry, Faculty of Education, Ain Shams University, Egypt

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POLYSILOXANE-IMMOBILIZED TRIAMINE LIGAND SYSTEM, SYNTHESIS AND APPLICATIONS

Issa M. El-Nahhal,[a] *Basheer A. El-Shetary,*[b] *Kamal A. R. Salib,*[b] *Nizam M. El-Ashgar,*[a] *and Ahmed M. El-Hashash*[a]
Department of Chemistry, Al-Azhar University, PO Box 1277, Gaza, Palestine[a] *and Department of Chemistry, Faculty of Education, Ain Shams University, Egypt*[b]

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The polysiloxane-immobilized triamine ligand system of the formula $P\text{-}(CH_2)_3NH(CH_2)_2NH(CH_2)_2NH_2$ *(where P represents the siloxane network) has been prepared via the sol-gel process by hydrolytic polycondensation of* $(EtO)_4Si$ *and* $(MeO)_3Si(CH_2)_3NH(CH_2)_2NH(CH_2)_2NH_2$*. An alternative method was used by the reaction of the iodopolysiloxane* $P\text{-}(CH_2)_3\text{-}I$ *and diethylenetriamine in the presence of triethylamine. The immobilized triamine ligand forms metal chelate complexes when treated with aqueous metal(II) ion solutions (*Co^{2+}*,* Ni^{2+}*, and* Cu^{2+}*). The elemental analysis and FTIR results suggest that this ligand system undergoes a substantial leaching of diethylenetriamine ligand moieties from the siloxane framework.*

Keywords: Metal uptake; polysiloxanes; polysiloxane-immobilized ligand systems; triamine ligands

INTRODUCTION

The polysiloxane-immobilized triamine ligand systems are of great importance in science and industry because of the applications in many areas of research.[1,2] There are two procedures used for their preparation, first by the chemical modification of silica surface by anchoring an organofunctional alkoxysilane onto the silica surface.[3] The second method used is the sol-gel process by incorporation of the organofunctional alkoxysilane with the tetraethylorthosilicate (TEOS).[4–11] Many ligand groups have been introduced to the polysiloxane framework include, amines,[7] thiols,[4] phosphines,[8] iminodiacetates[9] and glycinates.[10] The immobilized ligand systems have several applications in the

Address correspondence to Issa M. El-Nahhal, Department of Chemistry, Al-Azhar University, PO Box 1277, Gaza, Palestine. E-mail: issaelnahhal@hotmail.com

analytical field (e.g. stationary phases in chromatography,[12] adsorption and removal of heavy metal ions).[13–16] Heterogeneous catalysts[8,17] are also prepared which combine the advantages of activity and selectivity of homogeneous catalysts. These materials also have several biological applications as immobilized supports for enzymes.[18–21]

Several research workers[22,23] have based their characterization of the immobilized ligand systems on using elemental analysis and classical spectroscopic methods, which lack the efficiency to give complete information about their structures. Recently high resolution solid-state NMR techniques,[24–27] which include ^{29}Si, ^{15}N, ^{13}C, and ^{1}H NMR give valuable information about the molecular structures. One important type of the polysiloxane-immobilized ligand systems are those of the amines, which have been used for preconcentration, and removal of heavy metal ions. In our last publications, detailed investigations of the immobilized monoamine and diamine are reported.[28,29]

In this work the immobilized triamine ligand system is prepared, characterized and used for preconcentration of divalent metal ions (Co^{2+}, Ni^{2+}, and Cu^{2+}).

EXPERIMENTAL

Chemicals and Reagents

All starting materials including tetraethylorthosilicate ($(EtO)_4Si$, 3-diethylenetriaminepropyltrimethoxysilane, and 3-iodopropyltrimethoxysilane were purchased from (MERCK) and used as received without further purification. Acetone and diethylether were dried by storing over anhydrous sodium sulphate for three days, then distilled. All standard solutions of metal ions (Co^{2+}, Ni^{2+}, and Cu^{2+} were prepared from their chloride salts, analar grade) by dissolving a known amount of the salt in distilled water to the appropriate range of ion concentration (ppm). Lower concentrations were obtained by dilution. Acetate buffer was prepared using acetic acid/sodium acetate of pH (4–6). Lower pH solutions (pH 1–3) were prepared by adding 0.5 M HCl to the acetate solution.

General Techniques

Analysis for carbon, hydrogen, and nitrogen were carried out using Elemental Analyzer EA 1110-CHNS CE instrument. The infrared spectra for the immobilized triamine were recorded on a SHIMADZU FTIR - 8201PC, spectrophotometer using KBr disk in the range 4000 to

400 cm^{-1}. The metal ion concentrations in aqueous solutions were measured using a Perkin-Elmer AAnalyst-100, spectrotometer. The appropriate absorbance reading for each metal ion was obtained by diluting the sample with distilled water to the optimum analytical range for each metal. The standard solutions for each metal ion were also prepared using distilled water to construct the calibration curves for the metal ions. All pH measurements were obtained using WTW 521 pH meter.

Preparation of 3-Iodopropylpolysiloxane (PI)

The iodopropylpolysiloxane was prepared as previously described[11,29] by adding (14.5 g, 0.05 mol) of 3-iodopropyltrimethoxysilane to (20.8 g, 0.1 mol) tetraethylorthosilicate in 20 cm^3 methanol while stirring, followed by 4.95 cm^3 HCl, 0.42 M as a catalyst. The mixture was kept with stirring for 24 h, gelation occurred and a gelatinous material was obtained. The product was dried, crushed, sieved, washed with successive portions 50 cm^3 of water, methanol, and diethyl ether. Finally the product was dried for 12 h at 100°C and 15.0 g of the solid material was obtained.

Preparation of Immobilized Triamine Ligands (PT$_1$ and PT$_2$)

From Iodopolysiloxane (PT$_1$)

The immobilized triamine ligand system (PT$_1$) was prepared by the reaction of 5 g of iodopolysiloxane with excess of diethylenetriamine. The mixture was refluxed for 72 h at 120°C. The material was filtered and washed with successive portions, 30 cm^3, of 0.025 M NaOH, distilled water, methanol, and diethyl either. The product was dried in vacuum (0.1 torr) at 90°C for 12 h and 4.80 g of the solid material was obtained.

From the Sol-Gel Method (PT$_2$)

This functionalized polysiloxane was prepared by dissolving tetraethylorthosilicate (20.83 g, 0.1 mol) in 15 cm^3 methanol and 4.95 cm^3 HCl, 0.42 M. The mixture was stirred at room temperature for a few minutes. 3-Diethylenetriaminepropyltrimethoxysilane (13.27 g, 0.05 mol) was added as one portion to the stirred mixture. Gelation occurred in a few seconds, the product was left to stand for 12 h. The product was dried in a vacuum oven at 90°C, crushed, sieved, and washed with successive portions, 50 cm^3 of 0.025 M NaOH, distilled water, methanol, and diethyl ether, and then dried in a vacuum oven (0.1 torr) at 90°C for 10 h.

Metal Uptake

General Procedure

A known amount of the functionalized polysiloxane, PT_2, (100 mg) was shaken with an aqueous solution of the appropriate metal(II) ion (Co^{2+}, Ni^{2+}, and Cu^{2+}) using stoppered 250-ml cylinder type bottles. Measurement of the metal ion concentration was carried out by allowing the insoluble complex to settle and an appropriate volume of the supernatant liquid was withdrawn using a micropipette then diluted to the optimum analytical range for atomic absorption analysis for each metal. The concentration of the original stock solution was also measured in the same way to obtain the initial concentration of the metal ion solution. The metal ion uptake for each ligand was calculated as mmole of M^{2+} per one gram of ligand.

Effect of pH

A 100 mg of the solid polysiloxane ligand was shaken with an aqueous solution of each of the divalent metal ions (25 cm^3, 0.02 M) at different pH values in the range 1–6 for Cu^{2+}, pH 1–7 for Ni^{2+} and Co^{2+}. The metal uptake was determined by analysis using the atomic absorption spectrometer.

Leaching Studies of Immobilized Triamine Ligand System

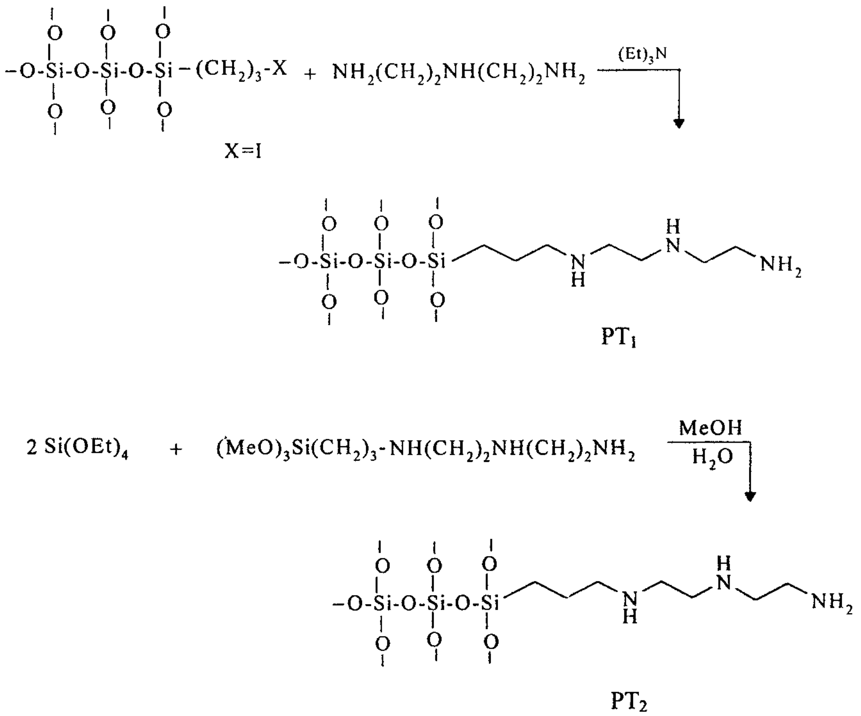
Effect of Cu^{2+} buffer solution. A 500 mg of polysiloxane immobilized triamine ligand was shaken with an aqueous solution of Cu^{2+} (100 cm^3, 0.02 M) using acetate solutions for 72 h. The solid material, was filtered, washed with dilute HCl (0.1 M), and dried in a vacuum oven at 100°C. The weight loss (%) was calculated as percentage of leaching versus pH.

Effect of pH without Cu^{2+} metal ion. A 500 mg of the polysiloxane immobilized triamine ligand was shaken with acetate solutions for 72 h. The ligand was filtered dried in vacuum oven at 100°C. The weight loss (%) of the ligand was calculated as a percentage of leaching versus pH.

RESULTS AND DISCUSSION

Synthesis of the Polysiloxanes

The diethylenetriamine ligand group can be introduced into the siloxane network either by the reaction between halogenofunctionalized polysiloxane and diethylenetriamine[24,30] or by hydrolytic polycondensation of $Si(OEt)_4$ and $(MeO)_3Si(CH_2)_3{-}NH(CH_2)NH(CH_2)_2NH_2$ as given in Scheme 1. The microanalysis results are listed in Table I.



SCHEME 1

In the former reaction (PT$_1$), the results given in Table I showed lower C, H, and N percentages than the expected values. This is probably due to steric hindrance effect, which leads to incomplete reaction, thus, only part of the iodide was substituted by diethylenetriamine.

TABLE I Elemental Analysis Data for the Iodopolysiloxane and the Polysiloxane-Immobilized Triamine Ligand Systems (PT$_1$ & PT$_2$)

Compound	Element	C%	H%	I%	N%	C/N	mmol N/g
PI	Found	9.0	2.2	32.3	—	—	—
PT$_1$	Expected[a]	22.5	5.6	0.0	11.7	2.5	7.6
	Found	16.5	4.5	15.3	5.6	3.4	4.0
PT$_2$	Expected[b]	26.5	5.69	—	13.29	2.33	9.49
	Found	21.00	6.20	—	10.20	2.40	7.28

[a] The expected values of PT$_1$ were calculated based on the found iodine percentage of the iodopolysiloxane.

[b] The expected values for PT$_2$ were calculated based on the stiochiometry of reactants assuming complete hydrolysis and polycondensation.

In the second method, the polysiloxane-immobilized triamine ligand system (PT_2) was prepared by hydrolytic polycondensation of tetraethylorthosilicate (TEOS) and 3-diethylenetriaminepropyltrimethoxysilane. Methanol was added to the mixture to make a homogeneous mixture, followed by the calculated amount of water to hydrolyze the alkoxy groups. The results indicate that the percentages found of C and N are lower than those expected for the reaction stoichiometry. This can be expected due to the formation of small oligomers, which are water-soluble and are lost during washing process.[11,26] These small oligomers are a non-cross-linked particles which formed due to the different rates of hydrolysis of the starting silane agents.[4,11,25,28] The results show that, the carbon to nitrogen ratio is very close to the expected one. This may explain that oligomers containing organofunctional groups were leached from the polymeric matrix.[4,25]

FTIR Spectra

The FTIR spectrum for the polysiloxane immobilized triamine ligand system (PT_2) shows a strong adsorption band, in the range of 900–1200 cm^{-1}, which consists of three components at 951 cm^{-1}, 1086 cm^{-1}, and 1188 cm^{-1} due to ν(Si—O) stretching vibrations.[31–33] A strong broad band is also observed around 3456 cm^{-1}, due to ν(O—H) stretching vibrations. No distinctive bands appear for ν(N—H) because of the complicated structure of the polymer and the presence of hydrogen bonding between amine groups and surface silanol groups. A weak band at 1632 cm^{-1} appears which is due to δ(N—H) and/or δ(O—H) bending vibrations.

Proton Uptake Capacity of PT_2

The proton uptake (mmol H^+/g ligand) was studied for polysiloxane-immobilized triamine (PT_2) ligand system. Comparison between the capacity results and the nitrogen percentage based on elemental analysis are given in Table II.

TABLE II Proton Uptake Capacity for the Immobilized Triamine System (PT_2)

Ligand	mmol H^+ per gram of the ligand						mmol N/g
System	1 hr	2 hrs	5 hrs	10 hrs	24 hrs	48 hrs	—
PT_2	9.14	10.30	10.66	11.04	11.42	11.42	7.3

From Table II, it is obvious that the proton uptake increases with time. It is found that the mmol of protons taken by polysiloxane triamine (PT_2) is higher than values obtained from nitrogen analysis. This could be explained due to the acid hydrolysis of (Si—O—Si) siloxane linkages, and therefore some Si—OH bonds formed consuming a significant amount of protons.

Metal Uptake

Effect of the Exposure Time

The uptake of polysiloxane-immobilized triamine ligand towards metal ions (Co^{2+}, Ni^{2+}, and Cu^{2+}) was determined by shaking the ligand with each of the aqueous solution of metal ions at different time intervals. The results are given in Figures 1–3. It is shown that the metal ion is increased as a function of time. The increase of the uptake of metal ions within the first few hours is attributed to diffusion factors. The decrease of metal ion capacity after reaching maximum uptake, in particular in the case of copper and nickel solutions, is attributed to leaching and degradation of functionalised ligand groups from the siloxane network. It is found that the degree of degradation decreases from ($Co^{2+} < Ni^{2+} < Cu^{2+}$). In general the maximum metal uptake capacity for the immobilized triamine ligand system is greater than

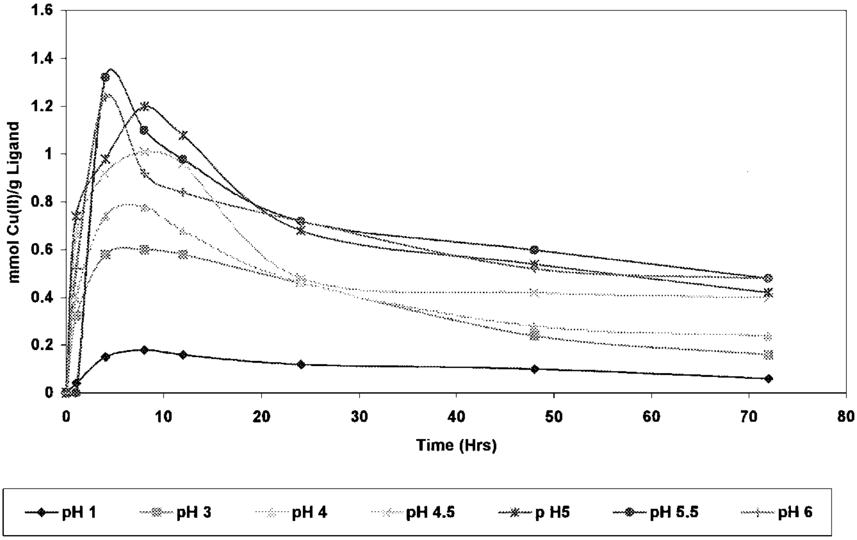


FIGURE 1 Uptake of Cu^{2+} ions by polysiloxane immobilized triamine ligand system (PT_2) versus time at different pH 1–7 (HCl/acetate solutions).

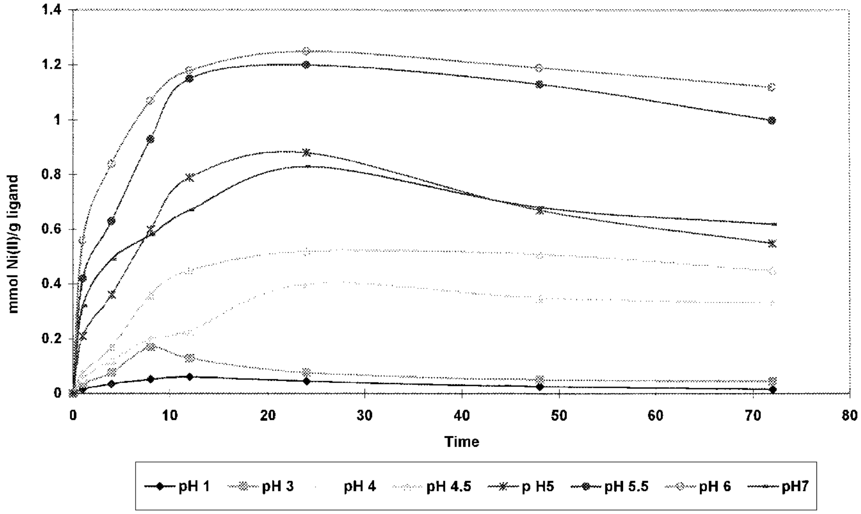


FIGURE 2 Uptake of Ni^{2+} ions by polysiloxane immobilized triamine ligand system (PT_2) versus time at different pH 1–7 (HCl/acetate solutions).

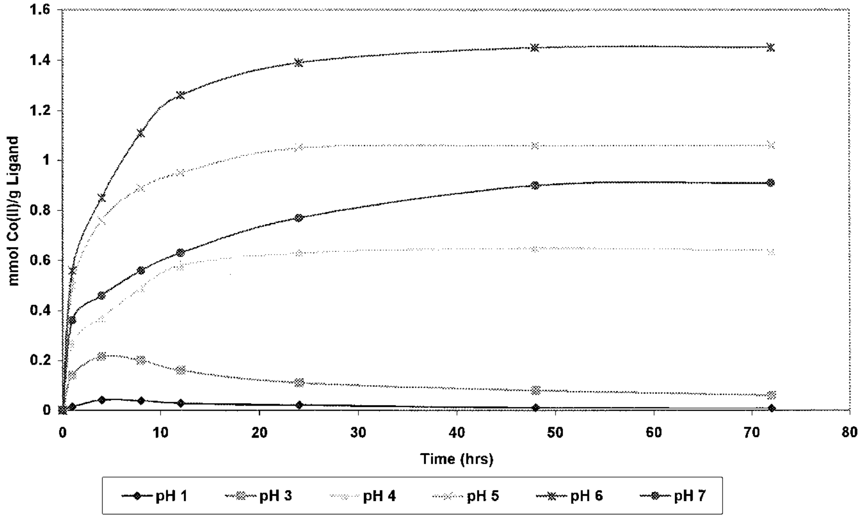


FIGURE 3 Uptake of Co^{2+} ions by polysiloxane immobilized triamine ligand system (PT_2) versus time at different pH 1–7 (HCl/acetate solutions).

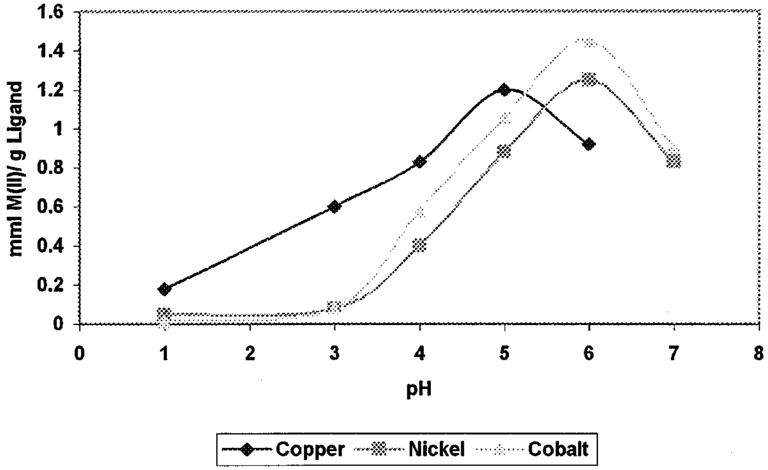


FIGURE 4 Uptake of Cu^{2+}, Ni^{2+} and Co^{2+} metal ions pypolysiloxane immobilized triamine ligand system (PT_2) versus pH 1–7 (HCl/acetate solutions).

the immobilized diamine ligand system[29] and those triamine ligands immobilized on silica surfaces.[4]

Effect of pH

The uptake of Cu^{2+}, Ni^{2+}, and Co^{2+} ions was examined at different pH values (1–6) and after 8 h shaking. The results are given in Figure 4. It is obvious that the recovery of each metal ion is very low at low pH and reaches its maximum uptake at pH 5 in case of Cu^{2+} and pH 6 in case of Ni^{2+} and Co^{2+}. This is consistent with reported results of similar ligand systems.[28,29]

The low uptake capacity at $\text{pH} < 4$ is mainly due to the protonation of the amine moieties. At $\text{pH} > 6$ the uptake of metal ions decreases due to formation of metal hydroxide.[28,34,35] The preferential adsorption of the three metal ions on PT_2 appeared to be in the following order:

$$\text{Cobalt} > \text{Nickel} \geq \text{Copper}$$

Stability of Polysiloxane-Immobilized Triamine Ligand System (PT_2)

Effect of Aqueous Buffered Solution

The stability of the polysiloxane-immobilized triamine ligand system was examined in the acetate solutions at different pH (1–7) at two different time intervals (72 and 120 h). The gravimetric analyses of the leaching materials into the solution are given in Figure 5. It

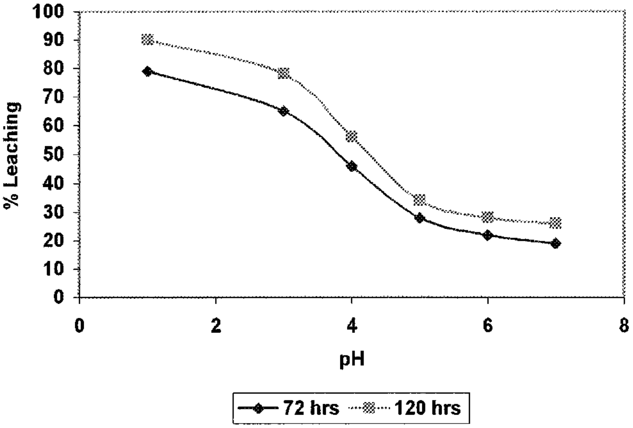


FIGURE 5 Leaching percentage of PT_2 versus pH values (acetate solutions, 72 and 120 h shaking time).

is clear that substantial portion of PT_2 leached into solutions especially at low pH. This is probably due to hydrolysis of siloxane network (Si—O—Si). Similar results were reported for monoamine.[28] and diamine[29] polysiloxanes in which less degree of degradation occurred. In these systems the amine groups act as self catalyzed and results in rapid gelation in which less rigid siloxane network[4,7,11] is formed. Therefore these ligand systems exhibit a great deal of hydrolysis upon treatment with acidic solutions. The amount of material leached as a function of time using acetate solutions is also examined. The results are given in Figure 6.

The elemental analysis of the polysiloxane-immobilized triamine ligand system treated with the acetate solutions at different pH values are given in Table III. Upon treatment with acidic solutions, the C, H, N

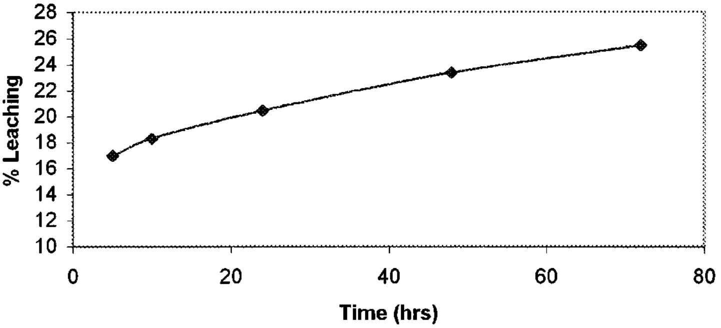


FIGURE 6 Leaching percentage of PT_2 versus time (acetate solution, pH 5.5).

TABLE III Elemental Analysis of Polysiloxane-Immobilized Triamine Ligand at Different pH Values (Using Acetate Solutions, 120 h Shaking Time)

Element	C%	H%	N%	C/N	mmol N/g
Expected[a]	26.5	5.7	13.3	2.3	9.5
Found (pH 7)	21.0	6.2	10.2	2.4	7.3
Found (pH 5)	14.4	4.6	5.8	2.9	4.2
Found (pH 4)	12.0	3.9	4.3	3.3	3.1
Found (pH 3)	10.6	3.7	3.8	3.3	2.7

[a] The expected values were calculate based on the stoichiometry of the reactants.

percentages decreases as the pH of the solution decreases. This is obviously due to leaching of ligand containing moieties from the siloxane surface especially in the acidic medium. The similar C/N values provide strong evidence that a ligand containing a group of seven carbon and three nitrogen atoms is leached out into the solution upon treatment with an acidic solution.[28]

Effect of Cu^{2+} Buffered Solution

The stability of polysiloxane-immobilized triamine ligand system (PT_2) was examined gravimetrically upon treatment with copper(II) solution (0.020 M) at different pH values. The leaching results at different pH values are given in Figure 7. It is obvious, that most of the PT_2 ligand is leached and dissolved completely at lower pH. From these results and those from the treatment with acetate buffer only, it is possible to suggest that the presence of copper ions facilitates and enhances the degradation of PT_2 ligand system. The change of the color from pale blue to deep blue is strong evidence that the leached functionalized

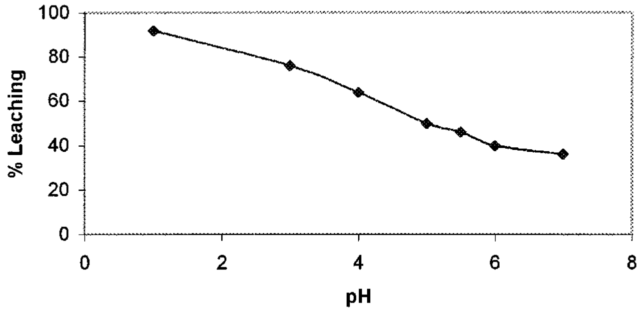


FIGURE 7 Leaching percentage of PT_2 versus pH of Cu^{2+} aqueous solutions (acetate solutions, pH 1–7, 120 h shaking time).

ligand groups formed soluble copper complex. The results obtained in the present work were supported by the results investigated by El-Nahhal and coworkers.[25,28,29]

CONCLUSION

The polysiloxane-immobilized triamine ligand system was prepared by two different routes: a hydrolytic polycondensation the triamine silane coupling agent and TEOS and by modification of iodopolysiloxane with diethylenetriamine. The immobilized triamine ligand system exhibit high potential for extraction of divalent metal ions (Co^{2+}, Ni^{2+}, and Cu^{2+}) from aqueous solutions forming metal(II) chelate complexes. The elemental analysis, FTIR and other chemical analysis suggest that this ligand system undergoes substantial degradation upon treatment with acidic solutions.

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